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Limiting law theory for light scattering in dispersions of charged spheres

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Abstract. A limiting law theory for the interpretation of light scattering photon correlation measurements in a dispersion of charged spherical particles is developed through the use of a cluster expansion technique. The methods used allow us to include the effects of the counter-ions in a more fundamental way than has been previously done; we find that these do not contribute in any significant way to the limiting law results. For values of the scattering vector usually considered we also find that only autocorrelation effects are important.

1. Introduction

The technique of photon correlation spectroscopy (PCS) has recently been applied to dispersions of charged spherical polystyrene particles (Brown *et al* 1975). An approximate theory for this experiment, in which the interactions between the particles are implicitly treated, has been developed by Pusey (1975). In order to extend these results to include interactions in a more basic way we must contend with a formidable problem; even if the fluid medium is treated as a structureless mediator we must still deal with two distinct types of particle-particle forces, due to charge and hydrodynamic interactions, and both of these forces are long ranged. For the case of uncharged particles a formal theory has been developed (Deutch and Oppenheim 1971), but even in this simpler case utilization of these results requires considerable approximations (Altenberger and Deutch 1973) and the results obtained are only described as 'primitive'. Further, in its present form this theory does not appear to be applicable to charged systems without the use of additional, uncontrollable assumptions (Badiali and Rosinberg 1973, Rosinberg 1973). There does however exist a proven theoretical framework in which both hydrodynamic and charge interactions can be treated. This is the cluster expansion theory developed by Friedman (1964a) who used this theory together with a Brownian model (Friedman 1964b) to obtain a statistical mechanical theory for the lowest-order concentration-dependent correction to the ohmic conductance in an ionic solution. This correction, which is not simply proportional to the ion concentration, is referred to as the limiting law for the conductivity; limiting laws exist for both thermodynamic and transport properties.

In this paper we will adopt Friedman's formalism and model to develop the limiting law theory for an idealized PCS experiment (see below). A distinct advantage of using these methods is that counter-ion effects are routinely included in the results which we

obtain and their contribution can be thus readily assessed. In particular, we will be interested in extending the result of Pusey (1975) which generalizes the infinite-dilution limit. We will simplify matters at the outset by considering a somewhat idealized system so as to be able to focus our attention on determining the dominant contributions to the limiting law theory. Thus, the actual experimental system has three components, the fluid medium (solvent hereafter), charged spherical particles (particles), and counterions (ions), and we will idealize by assuming:

- (i) The particles are mono-disperse and the charge on each is ze with $|z| \gg 1$.
- (ii) This charge is constant in time.
- (iii) The bare potential between all particles and ions is Coulombic; the ions and particles are point charges.

The first two assumptions require little comment. The first serves to eliminate tedious book-keeping and algebra and allows the more interesting facets of the problem to emerge, while the second is already implicit in most treatments of this problem (Stephen 1971, Phillies 1974) and is included here only because we feel that the theory of particle charge fluctuations is an interesting problem in its own right which deserves future study. We would not expect these fluctuations to contribute any significant effect to our present results, however.

The third assumption relates to our basic description of the system in which the ions are treated on an equal footing with the particles. Previous attempts to include the ions have either neglected particle-particle interactions (Ermak and Yeh 1974) or included the latter (more precisely the Coulombic part of this interaction) while treating the ions as a shielding background (Phillies 1974). We believe that the formalism adopted here allows a more fundamental and complete description to be obtained. Since the field produced by a uniformly charged particle is the same outside that particle as a point charge located at the particle centre, and since the ions and the particles are excluded by a hard core from the ion and particle interiors, we feel that this assumption is quite justified. It is not necessary for the limiting law theory to include these hard-core potentials (Phillies 1974) since they only contribute in higher order (in the particle concentration).

In what follows we will be guided in assessing the relative importance of particular terms in the results we obtain by the conditions which are found in the experiment of Brown *et al* (1975). We begin our theoretical development in § 2 by briefly outlining the salient features of Friedman's (1964a,b) results and showing how they apply in the present situation. In § 3 we obtain an explicit expression (equation (4)) for the limiting law correction to the infinite-dilution theory. A discussion of our results follows in § 4.

2. Cluster expansion for Brownons applied to PCS studies

The system of interest is composed of a dilute dispersion of particles and ions; the former each carry a charge of magnitude $q = |z|e$ with $|z| \gg 1$ and the latter a charge $\bar{q} = e$. Overall charge neutrality holds so that $cq = \bar{c}\bar{q}$, where c and \bar{c} are the concentrations of the particles and ions, respectively, and therefore $c \ll \bar{c} \ll 1$, this last inequality being an experimental condition. The notation used above will be followed throughout, a 'naked' symbol being used to denote a particle property and an overbar to denote the corresponding ion property. Greek subscripts will imply summation over both particles and ions, e.g. $\sum_{\alpha} q_{\alpha} = q + \bar{q}$, and Latin subscripts will indicate a sum over the particles only.

A fundamental quantity for the PCS experiment is $|g(\mathbf{K}, \tau)|$, the modulus of the normalized temporal autocorrelation function of the scattered electromagnetic field (Oliver 1974); \mathbf{K} is the scattering vector and τ the correlation delay time. For τ short enough so that

$$K \int_0^\tau dt' v_x(t') \ll 1 \quad (1)$$

we have (cf Pusey 1975, equation (12))

$$\frac{d}{d\tau} |g(\mathbf{K}, \tau)| = -\frac{K^2}{NS(K)} \sum_{a,b} \int_0^\tau dt \langle v_{ax}(0) v_{bx}(t) \exp[i\mathbf{K} \cdot (\mathbf{R}_a(0) - \mathbf{R}_b(0))] \rangle \quad (2)$$

where N is the number of particles, $S(K)$ is the static structure factor, $\mathbf{R}_a(t)$ is the position of particle a at time t and $v_{ax}(t)$ is its velocity component in the x direction which we will take along \mathbf{K} ; note according to our notation convention the above sum is over the particle velocities (and positions) only. The angular brackets denote a full ensemble average, over particles, ions, and the solvent. In lowest order in c the particles can be considered as non-interacting and their individual motions can be considered as that of pure Brownian motion at infinite dilution. Then only the autocorrelation terms, i.e. the $a = b$ terms, contribute to the above sum and we recover Pusey's (1975) result for the right-hand side of equation (2), $-K^2 D_0 / S(K)$, with D_0 the translational diffusion coefficient (this result is only strictly true if the integrand is essentially zero at $t \geq \tau$, which will be the case here (Harris 1975)). To be consistent $S(K)$ should also be expanded in c , but we will carry this through intact in what follows (see § 4).

In determining the first correction to the infinite-dilution result we will need to consider a systematic expansion of the right-hand side of equation (2) which makes use of c as a parameter of smallness. A formalism for carrying out such an expansion for the ohmic conductivity of an electrolytic solution has been given by Friedman (1964a). Apart from constant prefactors, the quantity which he expands is, in our notation,

$$\lim_{t \rightarrow \infty} \sum_{\alpha, \beta} \int_0^t dt' e^{-st'} \langle v_{\alpha x}(0) v_{\beta x}(t') \rangle.$$

This cluster expansion provides for the elimination of divergencies which would normally occur due to the long-range nature of the forces between particles, ions, and particle-ion pairs by a resummation procedure similar to that used in the equilibrium theory of ionic solutions to avoid identical problems (Friedman 1962). Neither the presence of the additional exponential term in the ensemble average on the right-hand side of equation (2) nor the fact that the sum there is limited to just one of the charged species, the particles, alter the arguments which justify the use of the cluster expansion so that we may also use it here as the basis of our expansion. In applying this formalism we must specify certain solvent-averaged quantities: a propagator describing motion in the solvent at infinite dilution and the many-body solvent averaged pair forces between the particles and ions are the basic quantities. In the Brownian model (Friedman 1964b) these are taken to be the propagator for Brownian motion and the longest-range part of the Coulomb force, screened by the solvent, and the Stokes force. The structure of the solvent is therefore ignored, as is the case at infinite dilution, and it is characterized only by its dielectric constant, ϵ , and viscosity, η . We will employ this model here also. One final (minor) point of clarification is called for. In this model, as in other work where the motion of the ions has been considered, the motion of the ions as well as that of the

particles is given in lowest order as a Brownian motion. Since the bare ions here are not massive compared to the solvent molecules, this would appear at first sight to be blatantly incorrect. However, in solution the ions will be solvated so that the basic charge carrier will have a considerably larger mass than a solvent molecule, and its motion can be described as Brownian (with an appropriate radius, the Stokes radius, larger than the ion crystallographic value).

3. Limiting law results

3.1. Autocorrelation terms

The autocorrelation contribution to the sum on the right-hand side of equation (2) is particularly simple to determine since the exponential term is identically unity for this case and we are left with the bare velocity autocorrelation function. In the Debye-Huckel approximation we have (Harris 1973)

$$\begin{aligned} \mathcal{L} \frac{1}{N} \sum_a \langle v_{ax}(0)v_{ax}(t) \rangle \\ = \frac{1}{m\beta(s + \zeta/m)} - \beta \sum_{\alpha} \frac{4\pi c_{\alpha}}{3\kappa_D \epsilon^2} \frac{q^2 q_{\alpha}^2}{(\zeta + \zeta_{\alpha})} \frac{\zeta_{\alpha}}{\zeta} \frac{1}{[1 + (s/\omega_{\alpha})^{1/2}]} + O(c \ln c). \end{aligned} \quad (3)$$

Here κ_D is the Debye shielding parameter,

$$\kappa_D^2 = 4\pi\epsilon^{-1} \sum_{\alpha} c_{\alpha} q_{\alpha}^2, \quad \zeta_{\alpha} = 6\pi\eta R_{\alpha}$$

is the friction coefficient for charge species α , with R_{α} its radius, and $\omega_{\alpha} \equiv \kappa_D^2(\zeta^{-1} + \zeta_{\alpha}^{-1})/\beta$. We have used the Laplace transform, $\mathcal{L}f(t) = \int_0^{\infty} dt e^{-st}f(t)$ since the time dependence is most simply indicated this way.

For the first term on the right-hand side of equation (3), which is the infinite-dilution result, it is easily verified that for τ of interest, say $10^{-8} \text{ s} \leq \tau \leq 10^{-6} \text{ s}$, the τ limit in equation (2) can be replaced by infinity (Harris 1975). For the second term this is not readily apparent since this decays much slower, as $t^{-3/2}$ (Harris 1973); however this also turns out to be the case. Note, this slow decay is quite distinct in origin from that resulting from the use of a frequency-dependent friction coefficient in the description of infinite-dilution Brownian motion.

The contribution of the ions in the above result is through the sum, which includes both particles and ions as field particles, and through the Debye and ω_{α} parameters. However, when we take into account the inequalities $q \gg \bar{q}$, $R \gg \bar{R}$, together with the charge neutrality we find

$$\kappa_D^2 \approx \kappa^2 = 4\pi\beta c q^2 / \epsilon,$$

the shielding parameter with the ions neglected; the ion field term is also negligible. Since we can replace τ in equation (2) by infinity, the limiting law autocorrelation contribution in that equation is given from the $s \rightarrow 0$ limit of equation (3); denoting this by a superscript (1/2) to indicate the $c^{1/2}$ dependence, and a subscript A we have

$$\begin{aligned} \frac{d}{d\tau} |g(\mathbf{K}, \tau)|_A^{(1/2)} &= \frac{K^2 \beta}{S(K)} \sum_{\alpha} \frac{4\pi c_{\alpha}}{3\kappa_D \epsilon^2} \frac{q^2 q_{\alpha}^2}{\zeta + \zeta_{\alpha}} \frac{\zeta_{\alpha}}{\zeta} \\ &\approx \frac{K^2 \beta}{S(K)} \frac{4\pi c}{3\kappa \epsilon^2} \frac{q^4}{2\zeta}. \end{aligned} \quad (4)$$

The Debye–Huckel result can be improved by including the chain terms in the evaluation of the velocity autocorrelation function. This does not qualitatively affect the above result, leading only to an additional numerical prefactor of $(1 + 2^{-1/2})^{-1}$ which gives what we may refer to as the Onsager approximation (Friedman 1964b). The above result very clearly shows that the ion contributions to the autocorrelation part of the limiting law term are negligible.

3.2. Joint correlation terms

In evaluating the joint correlation contribution to the right-hand side of equation (2) we will have to include the exponential term which appears in the ensemble average. In lowest order and in the Debye–Huckel approximation we have

$$\begin{aligned} & \mathcal{L} \frac{1}{N} \sum_{\substack{a,b \\ a \neq b}} \langle v_{bx}(0) v_{ax}(t) \exp[i\mathbf{K} \cdot (\mathbf{R}_b(0) - \mathbf{R}_a(0))] \rangle \\ &= \frac{cq^2}{16\pi^4 \zeta m} \mathbf{u}_x \cdot \int_{-\infty}^{\infty} dz \int d\mathbf{k} \int d\mathbf{v}_a(t') \tilde{\mathbf{Q}}_{ab}^0(-\mathbf{k}, z) \cdot \mathbf{u}_x \\ & \quad \times \tilde{P}_a(\mathbf{k}, is - z) \mathbf{v}_b(0) W_a W_b \tilde{h}_{ab}^*(\mathbf{k}) d\mathbf{v}_a(0) d\mathbf{v}_b(0). \end{aligned} \quad (5)$$

To clarify this equation we have retained as far as possible the notation of Friedman (1964b); $\mathbf{v}_a(t)$ is the velocity of particle a at time t , W_a the normalized equilibrium velocity distribution function for $\mathbf{v}_a(0)$, $P_a(0, t)$ the propagator for particle a to go from $\mathbf{v}_a(0)$ to $\mathbf{v}_a(t)$ in the interval $(0, t)$ at infinite dilution, and

$$\mathbf{Q}_{ab}^0(0, t) = \int d\mathbf{R}_b(t) \int d\mathbf{v}_b(t) \mathbf{F}_{ab} P_b(0, t)$$

with \mathbf{F}_{ab} the solvent-averaged force on particle a due to particle b (we have mentioned above that it is the specification of P_a and \mathbf{F}_{ab} which defines the Brownian model). The Fourier–Laplace transform, indicated by a tilde, is used here:

$$\tilde{f}(\mathbf{k}, z) = \int_0^{\infty} dt e^{izt} \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} f(\mathbf{r}, t).$$

Finally, \mathbf{u}_x is the unit vector along \mathbf{K} , already taken to lie in the x direction. The remaining term,

$$h_{ab}^*(\mathbf{R}_a - \mathbf{R}_b) = h_{ab}(|\mathbf{R}_a - \mathbf{R}_b|) \exp[i\mathbf{K} \cdot (\mathbf{R}_b - \mathbf{R}_a)]$$

is the product of the lowest-order part of the equilibrium configuration correlation function, h_{ab} , and the exponential term so that

$$\begin{aligned} \tilde{h}_{ab}^*(\mathbf{k}) &= \int d\mathbf{R} \exp[i\mathbf{k} \cdot (\mathbf{R}_a - \mathbf{R}_b)] \exp[i\mathbf{K} \cdot (\mathbf{R}_b - \mathbf{R}_a)] h_{ab}(R) \\ &= \tilde{h}_{ab}(\mathbf{k} - \mathbf{K}) = -\frac{4\pi\beta q^2}{\epsilon[\kappa^2 + (\mathbf{k} - \mathbf{K})^2]} \end{aligned} \quad (6)$$

with $\mathbf{R} = \mathbf{R}_a - \mathbf{R}_b = \mathbf{R}_a(0) - \mathbf{R}_b(0)$.

The Coulombic and Stokes components of \mathbf{F}_{ab} each contribute separately to (5), however as they both lead to similar results we will only consider the first in detail here. Note first that all the integrals except that over \mathbf{k} can be carried out exactly as by Friedman (1964b), and that it is this remaining integration which determines the

concentration dependence. Calling this integral $I_c(s)$, we have

$$I_c(s) = \int d\mathbf{k} \frac{(\mathbf{u}_x \cdot \mathbf{k})^2 k^{-2}}{[k^2(2/\beta\zeta) + s][\kappa^2 + (\mathbf{k} - \mathbf{K})^2]} \quad (7)$$

which for $\mathbf{K} = 0$ is identical to Friedman's equation (4.12). Introducing spherical coordinates, this becomes

$$I_c(s) = \int_0^{2\pi} d\theta \cos^2 \theta \int_0^\pi d\phi \sin^3 \phi \int_0^\infty dk \frac{k^2}{[k^2(2/\beta\zeta) + s](\kappa^2 + K^2 + k^2 - 2Kk \sin \phi \cos \theta)} \quad (8)$$

We have been unable to evaluate this integral analytically, however it is possible to expand the integral by making use of the inequality of the means, $K^2 + k^2 \geq 2Kk$, and integrate term by term. For our present purposes this will suffice (equation (7) is also based on a similar expansion). Carrying out this procedure after taking the $s \rightarrow 0$ limit which is again appropriate, we have

$$I_c(0) = \frac{\pi^2 \beta \zeta}{3(\kappa^2 + K^2)^{1/2}} \left(1 + \frac{4}{5\pi} \frac{K^2}{\kappa^2 + K^2} + \dots \right). \quad (9)$$

The presence of the $(\kappa^2 + K^2)^{-1/2}$ term indicates that the Coulombic joint correlation term will not contribute to the limiting law for values of K of practical interest, e.g. in the experimental studies of Brown *et al* we find data reported over the range $0.6 \leq K \times 10^{-5} \leq 3.3$ and κ estimated at about 3×10^4 (all in cm^{-1}) for which case the Coulombic joint correlation term is negligible compared to the autocorrelation term.

We also find $\kappa \approx K$ from the expression for κ preceding equation (4).

The calculation of the Stokes component can be carried out in a similar manner, again resulting in a $(\kappa^2 + K^2)^{-1/2}$ dependence so that the entire joint correlation term will not contribute to the limiting law. In the next section we will see this combination of κ and K occurs also when we consider the concentration dependence of $S(K)$.

3.3 Conclusion

We have seen that only autocorrelation terms contribute to the limiting law for $d|g(\mathbf{K}, \tau)|/d\tau$. These terms are due solely to the Coulombic interaction between the particles, the contribution from the hydrodynamic interaction being identically zero. Thus we see that as the particle concentration increases from infinite dilution to the limiting law regime we must only consider the electrostatic interaction; this verifies an implicit assumption of Pusey's (1975) based on the strong structure evident in the experimental results (Brown *et al* 1975).

4. Discussion

4.1 Particle-particle interactions

In obtaining the above results we have used the Debye-Huckel (DH) value for the equilibrium configuration correlation function h_{ab} appropriate to our model of point charges; this is implicit in the second term of equation (3) and explicit in equations (6)–(9). As noted by Brown *et al* (1975, § 5.1) the conditions of their experiment are

such that the mean particle separation $c^{-1/3}$ is comparable to the separation length L at which the particle-particle interaction energy is equal in magnitude to the thermal energy kT . We would not expect the DH approximation for h_{ab} to be particularly good under such conditions; however, it is known that volume integrals of h_{ab} , e.g. for determining thermodynamic properties, are often quite accurate under conditions where h_{ab} itself is not. Our results would be best at more dilute concentrations for which $c^{-1/3} \gg L$. At significantly lower concentrations than those reported counter-ions due to the intrinsic ionization of the solvent would have to be included and our results would not apply without modification. This would not qualitatively alter our results however.

It is possible to modify our results to better accommodate the experimental conditions by using the potential

$$U(r) = \frac{\epsilon R^2 \psi^2}{r} \exp[-\kappa(r - 2R)] \quad (10)$$

(Brown *et al* 1975, § 5.1) for two particles separated by r to determine h_{ab} . A similar potential has been used by Phillies (1974) for just this purpose (note, we only require the particle-particle correlation function in our calculations). Since this only differs by a constant prefactor from the DH potential

$$U_{\text{DH}}(r) = (q^2/\epsilon r) e^{-\kappa r} \quad (11)$$

we can see immediately how this would modify our previous results. The joint correlation terms can still be ignored and in place of equation (4) we have

$$\frac{d}{d\tau} |g(\mathbf{K}, \tau)|_{\text{A}}^{(1/2)} \approx \frac{K^2 \beta}{S(K)} \frac{4\pi c}{3\kappa} R^2 \psi^2 \quad (12)$$

with ψ the surface potential.

The theory which supports $U(r)$ does not seem well enough developed at present to make it worthwhile to pursue this point here any further, and our opinion is that our present results, in the form of equation (4), are most useful at low dilution for which the point charge model in the DH approximation is a reasonable description. In future work we will consider alternative choices of h_{ab} , in the context of the charged sphere model which is most applicable here, based on recent results in the equilibrium statistical mechanical theory for such systems.

4.2. Final comments

Several interesting points which have emerged from this study bear comment on. First, our main result, equation (4), is similar to that found for uncharged systems (Altenberger and Deutch 1973) with D_0 being replaced by a concentration D_{eff} (in that case the correction goes as c). It is interesting to note that $D_{\text{eff}} < D_0$ in our result while in the case of uncharged particles $D_{\text{eff}} > D_0$ was found. While the latter equality may result from a more complete theory, it can be shown that including the next-order terms in the hydrodynamic interaction in the present theory leads to the former inequality. It is beyond the scope of the present paper to discuss uncharged systems, however it is important to re-emphasize a very basic difference between these and the charged systems studied here. As was pointed out in § 3.3, only electrostatic interactions contribute to the lowest-order concentration corrections here, and therefore a more

complete treatment of the hydrodynamic interaction, including back-flow effects, is not required.

We also see from equation (4) that no new K dependence enters in going from D_0 to D_{eff} . The possibility of such dependence entering our results when the consistent form of $S(K)$ is used can be readily dismissed; we have

$$\begin{aligned} S(K) &= 1 + c \frac{4\pi}{K} \int_0^\infty dR h(R) R \sin KR \\ &= 1 - c \frac{4\pi q^2 \beta}{\epsilon(K^2 + \kappa^2)} + \text{higher order in } c \end{aligned} \quad (13)$$

so that for the limiting law $S(K) = 1$ holds. For the experiments of Brown *et al* (1975) a similar result would follow using h as determined by the potential given in equation (10). The same conclusion, $S(K) = 1$, is not immediately obvious for this case, however, because of the large value of the surface potential term, and some contribution to their results from $S(K)$ might be expected.

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